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Sustainable Polyesters Derived from Glucose and Castor Oil: Building Block Structure Impacts Properties

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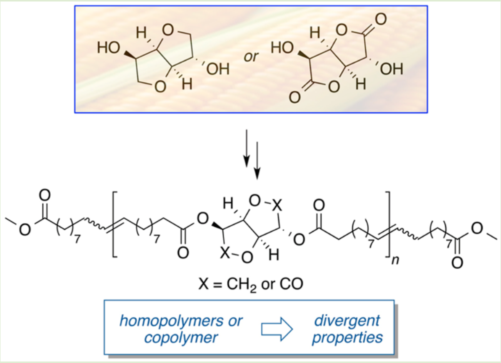
Ⓢ *Supporting Information*



ABSTRACT: Using the glucose derivatives isosorbide and glucarodilactone along with a castor oil derivative, 10-undecenoyl chloride, two monomers were synthesized: glucarodilactone undecenoate (GDLU) and isosorbide undecenoate (IU). These monomers were polymerized via acyclic diene metathesis (ADMET) polymerization to yield two homopolymers, P(GDLU) and P(IU), and two copolymers, P$_1$(GDLU-*co*-IU) and P$_2$(GDLU-*co*-IU), of similar number-averaged molecular weight and relative composition (51 and 61 kDa, *Đ* = 1.8 and 1.4, 46:54 and 52:48 mol percent). Comparison of the physical properties and degradation behavior of these polymers revealed divergent characteristics arising from differences in the nature of the carbohydrate building blocks. P(IU) is more thermally stable and has a lower glass transition temperature (T_d = 369 °C, T_g = −10 °C) than P(GDLU) (T_d = 206 °C, T_g = 32 °C) and P$_{1,2}$(GDLU-*co*-IU) (T_d = 210 and 203 °C, T_g = 1 and 7 °C). While all of the polymers were stable in acidic and neutral aqueous conditions, the two analogs containing GDLU hydrolytically degraded in the presence of base. Tensile testing of the systems revealed that both homopolymers are brittle materials while the P(GDLU-*co*-IU) is more tough. Notably, P$_{1,2}$(GDLU-*co*-IU) was found to be a rubbery material with a low Young's modulus (0.020 and 0.002 GPa, respectively), displaying an average elongation at break of 480 and 640%, and shape memory properties.

The development of sustainable polymers that are derived from renewable sources and have the ability to degrade within a reasonable time frame under appropriate conditions continues to be a formidable challenge.[1] Carbohydrates represent important building blocks in the development of new sustainable materials and are of great interest considering their large supply, rich stereochemistry, and high heteroatom content.[2] A well-studied example is isosorbide, which has been used in a multitude of polymer applications.[3,4] Of particular interest was a recent report of the acyclic diene metathesis (ADMET) polymerization[5−8] of isosorbide undecenoate, derived from coupling isosorbide with a castor oil derivative, to yield low molecular weight, sustainably derived polymers (**PIU**, Scheme 1).[9] While isomerizations that take place during ADMET were emphasized in this report, the properties of the synthesized polymers were not explored.

Glucarodilactone (GDL)[10] is a glucose derivative structurally related to isosorbide, but featuring ester rather than ether functionalities. GDL has been used as a polyol in the synthesis of polyurethanes,[11,12] a comonomer in poly addition reactions to form hydroxylated nylons,[13,14] and a core moiety in methacrylated thermosets.[15] In addition, GDL has been used to synthesize glycopolycations for nucleic acid delivery and has been shown to exhibit high efficacy and low toxicity in extensive studies of biological systems.[16−18] Notwithstanding these advances, GDL remains an under-utilized carbohydrate derivative with great potential in polymer chemistry. We envisioned that replacement of the isosorbide components by GDL units in ADMET polymers would result in disparate properties. To this end, we targeted analogous polymers **PIU** and **PGDLU** of similar molecular weights for synthesis and comparison, in addition to two copolymers comprising both building blocks **P(GDLU-*co*-IU)**. Details of the preparative results are reported herein, as well as the finding of notable and potentially useful differences in thermal, mechanical, and degradation behaviors between the GDL- and isosorbide-derived polymers. Interestingly, the copolymers were found to exhibit shape memory behavior[19−22] while having the advantage of being processed from solution or the melt.

The key monomers glucarodilactone undecenoate (GDLU) and isosorbide undecenoate (IU) were synthesized and purified similarly (Scheme 1). To circumvent base-catalyzed ring opening of GDL during functionalization, stoichiometric amounts of DMAP were used during the coupling reaction. Formation of the DMAP pyridinium salt in situ facilitated a successful coupling reaction without degradation. ADMET polymerization conditions similar to those reported previously were used (1.0 mol percent of Grubb's second generation catalyst[23] at 80 °C).[24] The molecular weights of the polymers

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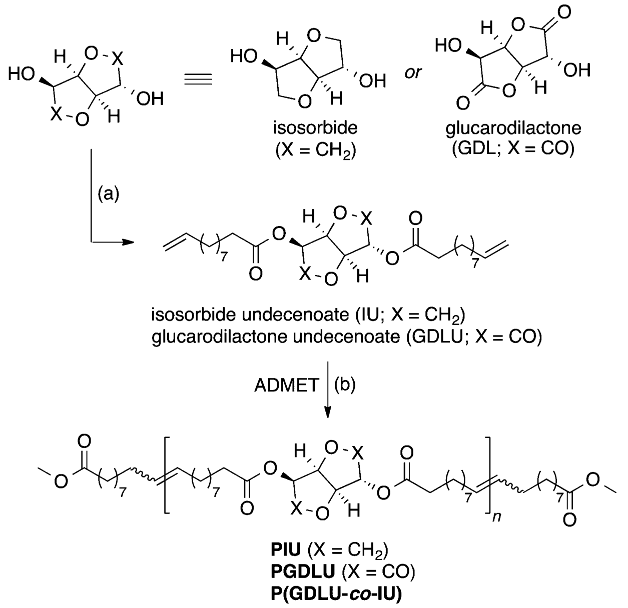
Scheme 1. Monomer and Polymer Syntheses[a]



[a]Reagents and conditions: (a) DMAP, 10-undecenoyl chloride, THF/CH_2Cl_2, 0 °C to RT, 16 h; (b) 1.0 mol % Grubb's 2nd generation catalyst, 1.0 mol % methyl 10-undecenoate, toluene (0.33M), 80 °C, 16 h, vacuum.

were controlled by the use of an end-capping reagent, methyl 10-undecenoate (1.0 mol %), which is the analogous methyl ester of the fatty acid chains used in the monomer. As noted elsewhere, using 1.0 mol % catalyst and 1.0 mol % end-capping reagent during the ADMET polymerizations formed high molecular weight polymers (Table 1),[24] albeit with a modified procedure involving the use of dynamic vacuum to facilitate the removal of coproduct ethylene.[25] The polymerization of the copolymer was performed twice, yielding **P_1(GDLU-*co*-IU)** and **P_2(GDLU-*co*-IU)**. The polymer molecular weights were characterized using ^{1}H NMR spectroscopy and size exclusion chromatography (SEC) with static light scattering (SLS), which revealed similar molecular weights for both copolymers. In all cases, signals for the capping methyl ester end groups were observed (δ = 3.67 ppm) and the vinyl end groups of the monomers were not present. In the case of **P_1(GDLU-*co*-IU)**, NMR analysis indicated a 46:54 ratio of isosorbide and GDL units. In the second batch of the copolymer, **P_2(GDLU-*co*-IU)**, NMR analysis indicated a 52:48 ratio of isosorbide and GDL units.

Table 1. Characterization Results for Illustrative Polymers

polymer ID	M_n[a]	$Đ$[b]	T_g[c] (°C)	T_m[c] (°C)	T_d[d] (°C)
PGDLU	61	1.8	32	59	206
PIU	56	1.8	−10	38	369
P_1(GDLU-*co*-IU)[a] (46:54 mol %)	51	1.8	1	24	210
P_2(GDLU-*co*-IU)[a] (52:48 mol %)	53[e]	1.4[e]	7	22	203

[a]kg/mol, determined by ^{1}H NMR. [b]Dispersity determined using SEC analysis. [c]Second heating glass transition and melting temperatures determined using DSC with heating and cooling rates of 10 °C/min. [d]Onset of degradation temperatures determined using TGA at 5% mass loss. [e]Determined via SEC-SLS analysis.

Thermogravimetric analysis (TGA) and hydrolytic degradation studies were conducted to examine polymer stability. TGA of **PGDLU** revealed an onset temperature of decomposition (T_d) of 206 °C with less than 5% weight loss up to T_d. By comparison, **PIU** was more thermally stable, with an onset temperature of degradation of 369 °C. The copolymers **$P_{1,2}$(GDLU-*co*-IU)** had comparable degradation temperatures to the homopolymer **PGDLU**. Interestingly, the copolymer with the slightly higher GDL ratio had a slightly lower decomposition temperature, indicating the copolymer stability was dependent on the GDL units in the polymer backbone. A similar trend in stability was found in hydrolytic degradation studies of the three polymers. In these experiments, polymers were cast from solution into the bottoms of 20 mL scintillation vials, water or aqueous solutions of HCl or NaOH were added, and the insoluble polymer mass was monitored over time (Figure 1). While all three polymers were hydrolytically stable under acidic and neutral conditions, subjection of **PGDLU** and **$P_{1,2}$(GDLU-*co*-IU)** to basic conditions resulted in relatively rapid degradation into water-soluble components; **PGDLU** degraded to approximately half of its original mass after 24 h, while the copolymers completely degraded in this time frame. Polymer swelling was not observed, giving credence to the fact that these polymers were not cross-linked. In the case of **$P_{1,2}$(GDLU-*co*-IU)**, the degradation products were identified by ^{1}H NMR spectroscopy as isosorbide and the disodium salts of glucaric acid and the metathesized repeat unit linkers (Scheme 2). In contrast to the polymers comprising GDL units, **PIU** was stable under all conditions examined, showing that the

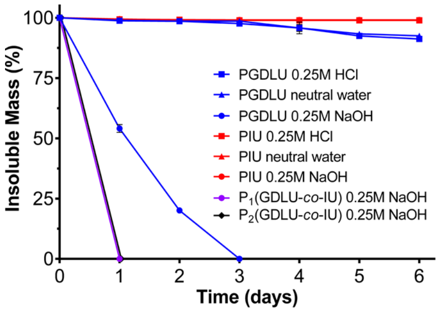
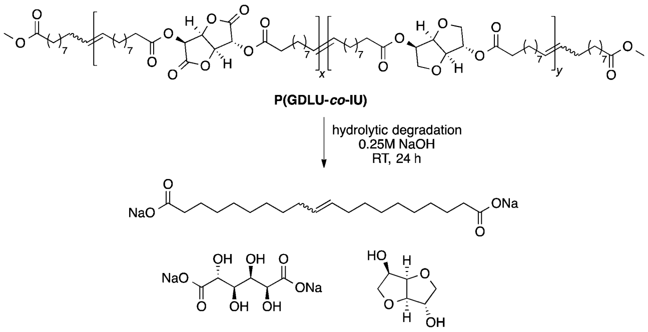


Figure 1. Polymer degradation studies over a six-day period. The values provided are an average of three replicates with the exception of **P(GDLU-*co*-IU)**, which was preformed in a single trial. Fresh portions of 0.25 M NaOH and HCl were used at the beginning of each 24 h period.

Scheme 2. Hydrolytic Degradation Products Resulting from Decomposition of P(GDLU-*co*-IU)



dilactone core is critical for hydrolytic degradation under basic conditions. Similar results were recently reported where dimethacrylate thermosets featuring GDL urethane linkages underwent hydrolytic degradation, whereas thermosets without GDL units were found to be stable under all conditions examined.[15]

The polymers were further analyzed using differential scanning calorimetry (DSC, Table 1, Figure S16). **PIU** exhibited the lowest T_g (−10 °C) and the greatest amount of crystallinity, as evidenced by a large melting endotherm at 38 °C. **PGDLU** was found to have higher T_g and T_m values, with the melting endotherm indicative of decreased crystallinity compared to **PIU**. Finally, after annealing, **P_1(GDLU-*co*-IU)** was found to be amorphous, as no melting endotherms were visible during the first heating cycle in the DSC thermogram. However, after the copolymer was allowed to cool at 10 °C/min during the cooling ramp between heating cycles (to −50 °C), a small melting endotherm at 24 °C was visible in the DSC thermogram. For **P_2(GDLU-*co*-IU)**, a small endotherm was observed in both heating cycles. In summary, the amount of polymer crystallinity as reflected by the DSC data is inversely correlated to the susceptibility to hydrolytic degradation. A similar correlation was noted previously for PLA, where increased crystallinity made the polymer more hydrolytically stable.[26,27]

Tensile testing experiments were performed to investigate the mechanical properties of the synthesized polymers. The tensile data for each of the polymers is summarized in Table S2, where mean values and errors for Young's modulus (E), ultimate tensile stress (σ), and elongation at break (ε) are reported from six replicate trials for each polymer sample. Representative stress versus strain curves are shown in Figure 2.

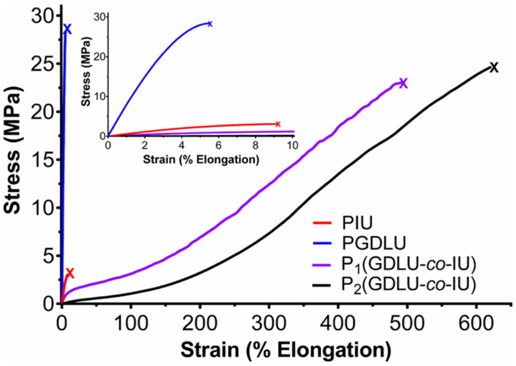


Figure 2. Representative stress vs strain curves for the homopolymers (top, inset) and the two copolymers. The representative curves were selected from six replicate trials. Tensile tests were performed at room temperature (25 °C) at a constant rate of displacement of 5 mm min^{-1}. "×" denotes the point of rupture as well as the ultimate tensile stress and strain at break. The **P_2(GDLU-*co*-IU)** sample required the constant rate of 50 mm min^{-1} to mitigate sample slippage from the instrument's grips.

The stress versus strain curves for each homopolymer show them to be brittle materials, consistent with their semicrystalline nature and the finding that **PGDLU** is a glass at room temperature (Figure 2, Table S2, Supporting Information). **PGDLU** exhibited properties of a tough material where the average ultimate tensile stress and modulus of elasticity were found to be 28 MPa and 0.74 GPa, respectfully. **PIU** was also brittle, but exhibited an average ultimate tensile stress of 3.2 MPa, almost an order of magnitude lower than that for **PGDLU**. At room temperature, **PIU** was a semicrystalline rubber, as reflected in the low modulus of elasticity of 0.059 GPa. In contrast to the homopolymers, at room temperature, the **$P_{1,2}$(GDLU-*co*-IU)** copolymers were found to be rubbery, amorphous materials with Young's moduli of 0.020 and 0.002 GPA, respectively. **P_1(GDLU-*co*-IU)** was stretched to a maximum average tensile stress of roughly 21 MPa and did not rupture until an average elongation at break of 480%. Interestingly, **P_2(GDLU-*co*-IU)** revealed a maximum average tensile stress of roughly 24 MPa and an average elongation at break of 640%. In addition, the copolymers demonstrated elasticity at low strain displacements. The possibility that the observed elastic behavior was due to chemical cross-linking (oxidative or otherwise) was examined by dissolving the copolymer in chloroform, passing the solution through a 0.20 μm syringe filter, and reanalyzing it using SEC. A comparable trace to the freshly synthesized sample was found, thus ruling out cross-linking. We speculate that the different tensile behavior of the homopolymers and the copolymers arises from differences in physical cross-linking semicrystallinity. The elastic behavior of the copolymer appears to result from the absence of crystallites in its microstructure. In essence, we hypothesizes that there is a "mismatch" between the crystalline isosorbide and amorphous GDL units in the copolymer that results in significant elasticity.

Following tensile testing experiments, it was observed that the elongated copolymer tensile bars would gradually return to their original shape at room temperature, which suggested the copolymer may have shape memory properties. These properties were examined further with a series of thermocyclical shape memory experiments, using a stainless steel metric ruler and neodymium bar magnets. After warming **P_1(GDLU-*co*-IU)** above its T_g in a 35 °C water bath, a 25 mm gauge rectangular bar was quickly elongated to an initial strain ($\varepsilon_{\text{initial}}$) of 200%. The neodymium bar magnets accurately and completely held the copolymer in place during the experiment. With the copolymer elongated in its deformed state, it was fixed in its temporary shape through quenching in an ice water bath. During cooling, it was observed that the polymer sample bar underwent a further slight (~8%) expansion, to a maximum strain ($\varepsilon_{\max}$) reached during each cycle of 208%. Elongation during cooling has been observed in previously reported shape memory polymers.[28,29] After the copolymer was fixed in the ice water bath for 3 min, the magnets were removed from the ruler, and the temporary shape was retained. The total strain was recovered (within seconds) when the deformed polymer was returned to the 35 °C water bath. After five heating and cooling cycles, the total strain recovery rate ($R_{\text{r,total}}$) was 89%, where the final strain ($\varepsilon_{\text{final}}$) after five cycles was 22% (Table S3, Supporting Information).

To further understand the mechanism of shape memory observed within these materials, thermocyclical shape memory testing was also performed at 50 °C using **P_2(GDLU-*co*-IU)**. The increased temperature in the heating cycle slightly altered the performance of the material revealing an $R_{\text{r,total}}$ of 77% after five heating and cooling cycles, and an $\varepsilon_{\text{final}}$ of 38% (Table S4, Supporting Information). In addition, the copolymer was able to recover greater than 99% of its deformed state after five cycles at both 35 and 50 °C. The strain recovery rate ($R_{\text{r},N-1}$) approached 100% after five cycles; the polymer chains likely become oriented in their elongated states from the temporary shape. We also observed the macroscopic shape memory effect of P_1(**GDLU-*co*-IU**) through deforming it to a temporary shape (spiral) and fixing it in an ice bath. Reheating the spiral regains the permanent shape (rod) of the sample (Figure 3). At this juncture the basis of the observed shape memory behavior is unclear, and in depth studies will be required in order to understand the relevant physical issues. In addition, future studies will investigate in depth the shape-memory properties and mechanisms of copolymers with varying compositions of GDLU and IU.

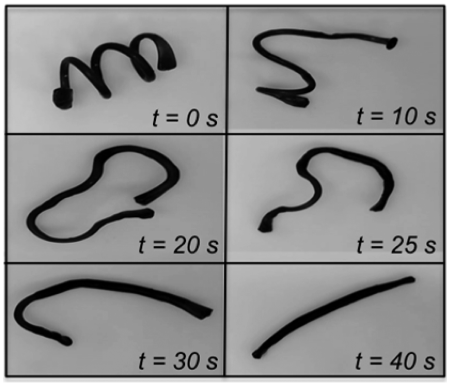


Figure 3. Photo series showing the macroscopic shape-memory effect in **P(GDLU-*co*-IU)**. The permanent shape was a long cylinder, and the temporary shape was a spiral. The spiral was removed from a 0 °C ice water bath, and placed on a Teflon sheet on a hot plate set to 35 °C. This experiment is also available as a movie in the Supporting Information.

In conclusion, the effects of variation in the sugar-derived building blocks in homo- and copolymers prepared via ADMET polymerization have been evaluated through studies of thermal, mechanical, and hydrolytic degradation properties. While **PIU** and **PGDLU** exhibited thermal and mechanical behaviors that diverged only slightly, distinctly different hydrolytic degradation rates for these homopolymers were observed (**PGDLU** > **PIU**). An even greater rate of degradation was observed for the copolymers $P_{1,2}$(**GDLU-*co*-IU**). The lactones in the GDL building blocks facilitate polymer degradation, which is an important criterion for future applications (i.e., biomedical devices). The thermal and mechanical properties of the copolymer **P(GDLU-*co*-IU)** differed significantly from those of the homopolymers comprising the same building blocks. Notably, the copolymer was amorphous and rubbery, with a high degree of elasticity quite different from the semicrystalline and brittle homopolymers. These differences may be attributed to lower degrees of crystallinity and potential differences in the compatibility of isosorbide and GDL subunits. We speculate that this incompatibility could be due to physical cross-linking via dipole interactions between the GDL units or partial lactone opening creating ionic (−COOH) and H-bonding (−OH) netpoints, which may contribute to the shape memory behavior of the copolymer, an intriguing property for sustainable polymers.[30] In sum, the work we describe herein highlights the complementary nature of isosorbide and GDL and illustrates the utility of GDL as a building block for renewable and degradable polymers.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details. ^{1}H and ^{13}C NMR spectra of the synthesized GDLU and IU monomers, ^{1}H NMR of the synthesized polymers and degradation products, SEC traces of the three synthesized polymers, TGA thermograms, DSC thermograms, mass loss data for hydrolytic degradation studies, and shape memory data for final strain after each cycle and strain recovery rates. In addition, a movie demonstrating the macroscopic shape memory effect of the copolymer is available. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Miller, S. A. *ACS Macro Lett.* **2013**, *2*, 550−554.
(2) Werpy, T.; Petersen, G. *Top Value Added Chemicals from Biomass*; PNNL: Richland, WA, 2004; Vol. *I*.
(3) Fenouillot, F.; Rousseau, A.; Colomines, G.; Saint-Loup, R.; Pascault, J. P. *Prog. Polym. Sci.* **2010**, *35*, 578−622.
(4) Feng, X.; East, A. J.; Hammond, W. B.; Zhang, Y.; Jaffe, M. *Polym. Adv. Technol.* **2010**, *22*, 139−150.
(5) Atallah, P.; Wagener, K. B.; Schulz, M. D. *Macromolecules* **2013**, *46*, 4735−4741.
(6) Yao, K.; Tang, C. *Macromolecules* **2013**, *46*, 1689−1712.
(7) Günther, S.; Lamprecht, P.; Luinstra, G. A. *Macromol. Symp.* **2010**, *293*, 15−19.
(8) Biermann, U.; Bornscheuer, U.; Meier, M. A. R.; Metzger, J. O.; Schäfer, H. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 3854−3871.
(9) Fokou, P. A.; Meier, M. A. R. *J. Am. Chem. Soc.* **2009**, *131*, 1664−1665.
(10) Gehret, T. C.; Frobese, A. S.; Zerbe, J. S.; Chenault, H. K. *J. Org. Chem.* **2009**, *74*, 8373−8376.
(11) Hashimoto, K.; Wibullcksanakul, S.; Okada, M. *J. Polym. Sci., Part A: Polym. Chem.* **1995**, *33*, 1495−1503.
(12) Hashimoto, K.; Wibullucksanakul, S.; Okada, M. *Makromol. Chem., Rapid Commun.* **1993**, *14*, 591−595.
(13) Kiely, D. E.; Chen, L.; Lin, T. H. *J. Am. Chem. Soc.* **1994**, *116*, 571−578.
(14) Chen, L.; Kiely, D. E. *J. Org. Chem.* **1996**, *61*, 5847−5851.
(15) Gallagher, J. J.; Hillmyer, M. A.; Reineke, T. M. *Macromolecules* **2014**, *47*, 498−505.
(16) Liu, Y.; Reineke, T. M. *J. Am. Chem. Soc.* **2005**, *127*, 3004−3015.
(17) Liu, Y.; Wenning, L.; Lynch, M.; Reineke, T. M. *J. Am. Chem. Soc.* **2004**, *126*, 7422−7423.
(18) Tranter, M.; Liu, Y.; He, S.; Gulick, J.; Ren, X.; Robbins, J.; Jones, W. K.; Reineke, T. M. *Mol. Ther.* **2012**, *20*, 601−608.
(19) Lendlein, A.; Kelch, S. *Agnew. Chem., Int. Ed.* **2002**, *41*, 2034−2057.
(20) Liu, C.; Qin, H.; Mather, P. T. *J. Mater. Chem.* **2007**, *17*, 1543−1558.
(21) Ratna, D.; Karger-Kocsis, J. *J. Mater. Sci.* **2007**, *43*, 254−269.
(22) Xie, T. *Polymer* **2011**, *52*, 4985−5000.
(23) Scholl, M.; Ding, S.; Lee, C. W.; Grubbs, R. H. *Org. Lett.* **1999**, *1*, 953−956.
(24) Rybak, A.; Meier, M. A. R. *ChemSusChem* **2008**, *1*, 542−547.

(25) Speros, J. C.; Paulsen, B. D.; White, S. P.; Wu, Y.; Jackson, E. A.; Slowinski, B. S.; Frisbie, C. D.; Hillmyer, M. A. *Macromolecules* **2012**, *45*, 2190−2199.

(26) Zhou, Q.; Xanthos, M. *Polym. Deg. Stab.* **2008**, *93*, 1450−1459.

(27) Tsuji, H.; Miyauchi, S. *Polym. Deg. Stab.* **2001**, *71*, 415−424.

(28) Yakacki, C. M.; Satarkar, N. S.; Gall, K.; Likos, R.; Hilt, J. Z. *J. Appl. Polym. Sci.* **2009**, *112*, 3166−3176.

(29) Xie, T.; Li, J.; Zhao, Q. *Macromolecules* **2014**, *47*, 1085−1089.

(30) Yamashiro, M.; Inoue, K.; Iji, M. *Polym. J.* **2008**, *40*, 657−662. Lu, X. L.; Sun, Z. J.; Cai, W.; Gao, Z. Y. *J. Mater. Sci.: Mater. Med.* **2008**, *19*, 395−399. Migneco, F.; Huang, Y.-C.; Birla, R. K.; Hollister, S. J. *Biomaterials* **2009**, *30*, 6479−6484. Guo, B.; Chen, Y.; Lei, Y.; Zhang, L.; Zhou, W. Y.; Rabie, A. B. M.; Zhao, J. *Biomacromolecules* **2011**, *12*, 1312−1321. Tsujimoto, T.; Uyama, H. *ACS Sustainable Chem. Eng.* **2014**, *2*, 2057−2062.

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